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SUPPLEMENTARY REPORT

AN EXTENSION OF THE STUDY ON FACTORS AFFECTING SO_2 AND NO_x EMISSIONS IN FLUIDIZED BED COMBUSTION

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1. INTRODUCTION

Recently, SO_2 and NO_x emission data from FBC combustors in Canada accumulated since the late seventies have been summarized and analyzed [1].

This report is an extension of the study of effects of fuel type and operating conditions on the SO_2 and NO_x emissions to fulfil requirements outlined by an amendment to the original contract.

The amendment specifies, for SO_2 emission, or equivalently the sulphur capture, a summary and examination of:

1) the effect of fuel minerals, especially the calcium content of the fuel,
2) the effect of superficial velocity,
3) the effect of limestone type,
4) the effect of limestone size, and
5) the effect of recycle.

Although the effects of limestone size and recycle were reported previously, (Section 4.2 in reference [1]). They will be presented here in terms of fraction of fuel sulphur captured rather than standardized SO_2 emission as in the previous report, since values of SO_2 emission are required to discuss the other variables.

For NO_x emission, the results presented in this report include:

1) the effect of fuel volatiles,
2) the effect of secondary to primary air ratio in circulating FBC tests, and

3) evaluation of previous models describing NO_x emission from fluidized bed combustors in terms of how well the models agree with the NO_x emission data.

2. ADDITIONAL INFORMATION ON THE OPERATING CONDITIONS

From the technical reports available [2-22], we have collected additional information including limestone type, limestone size, superficial velocity, and state of recycle. This information for pilot bubbling FBC tests with limestone addition is given in Table 1. Although the term recycle strictly interpreted means that all the cycloned material is returned to the bed, in some of the tests conducted at Queen's University, only a portion of the cycloned material was returned to the combustor. The values of the recycle fraction, defined as the fraction of cycloned dust that is returned to the combustor, are included where applicable. Information for Summerside tests is listed in Table 2 and information for circulating FBC tests is listed in Table 3. The values of the ratio of secondary to primary air are included in Table 3 for the circulating FBC tests. Information for tests where SO_2 emission data were not available is also included in these three tables since it is useful for the NO_x emission analysis. In order to provide a means of correlating the information to the previous summary, the numbering system for the tests and test programs used in the previous report [1] is employed in the three tables.

3. SO_2 EMISSION

3.1 EFFECT OF FUEL MINERALS IN BASE LINE TESTS

In addition to the sulphur content of the fuel, analysis of the data indicates that the emission of SO_2 observed in base line tests is affected by the mineral content of the fuel, especially calcium and magnesium which function as sorbents for SO_2. Figure 1 shows that the sulphur capture, expressed as averaged values over all runs performed for each test program, increases with the equivalent Ca/S molar ratio calculated so as to include both the calcium and magnesium content of the fuel. The detailed information for the base line tests is provided in Table 6 in the previous report [1].

Figure 1 also shows that the sulphur capture data obtained in the base line tests follow closely the empirical model derived from the tests with limestone addition given in the previous report, Section 4.7. The model so obtained is

$$Sr = 1 - 0.693*\exp[-0.329*(Ca/S)] \qquad (3.1)$$

where Sr is the fraction of the fuel sulphur captured, and Ca/S is the calcium to sulphur molar ratio. The model indicates that approximately 69.3% of the fuel sulphur is emitted as SO_2 in a sorbent-free test. It agrees well with the analysis of the effect of fuel sulphur on the SO_2 emission in base line tests which concluded that 71.5% of the fuel sulphur would be emitted as SO_2 in a sorbent-free test [1].

The data presented in Fig. 1 scatter significantly from the model suggesting an unexplained effect from compounds containing elements other than calcium or magnesium.

3.2 EFFECT OF FUEL VOLATILES IN SORBENT-FREE TESTS

Examination of Fig. 2 suggests that fuel volatile content has no consistent effect on the SO_2 emission in sorbent-free tests. No correlation exists between the volatiles content of the fuel and the sulphur capture expressed as averaged values over all base line tests performed for each test program. Tests with equivalent fuel Ca/S molar ratios larger than two, i.e., the tests with Highvale coal and Poplar River lignite, are excluded in this figure since these tests cannot be considered as sorbent-free tests.

3.3 EFFECT OF LIMESTONE SIZE

As discussed in Section 4.2 of the previous report [1], the limestone size has a significant effect on the efficiency of sulphur capture, and typical results for Minto coal tests were presented in Fig. 7 [1]. These data have been reinterpreted in terms of sulphur capture and the results are shown in Fig. 3 of this report.

Examination of Fig. 3 shows that for the Minto coal tests conducted at Queen's University, the lowest sulphur capture was observed in the test with 1.98 mm limestone without recycle. The

sulphur capture observed in the test with 1.98 mm limestone and a recycle fraction of 0.80, and the tests with 1.72 mm limestone and recycle fractions of 0.54-0.61 is well below that observed in the tests with 0.49 mm and 0.78 mm limestone, regardless of recycle fraction.

3.4 EFFECT OF RECYCLE

As demonstrated in the previous report, Section 4.2, the recycle system returns the elutriated limestone fines to the bed and reduces the average size of the in-bed limestone. Sulphur capture is thereby improved. This is especially true in the tests when limestone fines are added. Typical data are plotted in Fig. 8 in the previous report [1] for the Devco coal tests. These data are presented as sulphur capture in Fig. 4 of this report. For the tests conducted at Queen's University, the recycle fraction ranged between 0.67 and 0.86. In the tests with 0-6.3 mm limestone, which contains fine particles, the sulphur capture was particularly high when the recycle system was in operation. The data for the tests with 0-6.3 mm limestone and recycle are correlated to the Ca/S molar ratio as follows:

$$Sr = 1 - 0.807*\exp[-0.872*(Ca/S)] \quad (3.2)$$

For the remaining data in Fig. 4, the model is found to be

$$Sr = 1 - 0.807*\exp[-0.515*(Ca/S)] \quad (3.3)$$

The value of the coefficient reflecting the rate sulphur capture increases with the Ca/S molar ratio is larger in Eq. (3.2) than

that in Eq. (3.3), 0.872 compared to 0.515, indicating that a better efficiency in sulphur capture was achieved in the tests with 0-6.3 mm limestone and the recycle system in operation.

Figure 5 also shows the effect of recycle fraction. The sulphur capture observed in the tests with recycle fractions between 0.92 and 1.0 is correlated to Ca/S molar ratio by the model

$$Sr = 1 - 0.715*\exp[-1.099*(Ca/S)]. \quad (3.4)$$

Comparatively, the sulphur capture observed in the test without recycle, i.e., with zero recycle fraction, is considerably lower. The model to correlate these data is

$$Sr = 1 - 0.715*\exp[-0.643*(Ca/S)]. \quad (3.5)$$

The sulphur capture achieved in the tests with approximately half of the cycloned material returned to the bed, i.e., with recycle fractions between 0.56 and 0.64, does not show a noticeable difference from that without recycle. It appears that significant improvement in sulphur capture can be achieved only when a majority of the cycloned material returns to the bed.

It is also noted that two sizes of limestone were used in the tests with Evans coal conducted at Queen's University, i.e., 1.72 mm and 0.49 mm. The sulphur capture observed in the tests with full recycle is consistently high for both sizes of limestone. However, sulphur capture for tests without recycle or with approximately half of the cycloned material returned to the combustor was slightly lower when 1.72 mm limestone was used presumably due to the effect of limestone size.

3.5 EFFECT OF LIMESTONE TYPE

Since sulphur capture is affected by fuel type, limestone size and other operating conditions including the facility used, the effect of limestone type can be examined only in those tests with identical fuels and facility, and under similar operating conditions. These include: 1) the Devco coal tests conducted at Queen's University, 2) the Minto coal tests conducted at UBC, 3) the Syncrude coke tests conducted at Queen's University, and 4) the CANMET pitch tests with the Mark II combustor.

Figure 6 illustrates the sulphur capture observed in the Devco coal tests with three different kinds of limestone conducted at Queen's University. Since sulphur capture varies mainly with Ca/S molar ratio, the model derived from the data provides an average level of the sulphur capture for a given Ca/S molar ratio. Despite two major differences, for example, (1) the size of the Havelock limestone is slightly larger than the other two limestones, 1.72 mm compared to 1.4 mm and 1.1 mm, and (2) the recycle system was employed for the tests with Havelock limestone while the majority of the tests with Sysco and Calpo limestones were conducted without recycle, it is clear that little difference in the sulphur capture was found when the three different limestones were used in the tests.

In the Minto coal tests conducted at the UBC circulating FBC plant, the sulphur capture observed in the 1989 tests with Havelock limestone was higher than that observed in the 1987 tests with

Elmtree limestone. However, the difference is likely due to the modification of the plant between 1987 and 1989 rather than limestone type since the entire performance of the facility was improved after the modification [22].

The sulphur capture data for Syncrude coke and CANMET pitch tests are presented in Figs. 7 and 8, respectively. These data were presented as standardized SO_2 emission in Figs. 11 and 12 previously [1]. In Fig. 7, the results of tests with Havelock limestone agree well with the data for the tests with Athabasca limestone conducted in both the Queen's and the Mark II combustors.

In Fig. 8, the sulphur capture observed in the CANMET pitch tests with the Mark II combustor was found to be slightly lower when Athabasca limestone was used than when Havelock limestone was used. However, since the Athabasca limestone was much coarser, 0-6.3 mm compared to 0.85-2.36 mm for the Havelock limestone, the difference in sulphur capture was likely due to the limestone size rather than the limestone type.

3.6 EFFECT OF SUPERFICIAL VELOCITY

For bubbling FBC tests, both superficial velocity and the height of the bed affect the contact time of the SO_2 gas with the limestone. The effect of superficial velocity on sulphur capture, therefore, can best be examined in the tests conducted at Queen's University and at the Summerside heating plant where the bed heights were fixed. For the tests conducted at Queen's University,

we have only analyzed the tests with Minto, Devco and Evans coals. The results of the remaining test programs conducted at this plant do not provide valuable information with regard to the effect of superficial velocity because of the very narrow range of superficial velocity employed.

The results of the sulphur capture observed in the Minto and Devco coal tests conducted at Queen's University were shown in Figs. 3 and 6, respectively. The superficial velocity varied in the range 1.6-2.8 m/s for the Minto coal tests, and 1.5-2.7 m/s for the Devco coal tests. From those results, superficial velocity does not appear to significantly affect sulphur capture.

The results shown in Fig. 5 for the Evans coal tests conducted at Queen's University need more explanation. For the tests with 1.72 mm limestone, the sulphur capture observed in the three tests with recycle fractions between 0.92 and 0.97 shows little discrepancy from the model [Eq. (3.4)] despite the variation in superficial velocity (1.2-2.6 m/s). The superficial velocity for the test with part of the cycloned material returned to the bed and the test without recycle was in the range of 2.5-2.6 m/s. The sulphur capture observed in these two tests was slightly lower than the model prediction due to the operating state of the recycle system rather than the superficial velocity.

For the Evans coal tests with 0.49 mm limestone, our examination indicates that the difference in sulphur capture was also due to the status of the recycle system rather than superficial velocity. For example, despite the difference in

superficial velocity (1.6 m/s and 2.2 m/s, respectively), almost identical sulphur capture was achieved in the two no-recycle tests at Ca/S = 2.67 and 2.70. In fact, the superficial velocity for these three tests varied only in the narrow range 1.5-2.3 m/s.

Further, superficial velocity appeared to have no significant effect in the CANMET tests conducted at Summerside, Fig. 9. The lowest sulphur capture was observed in the test with Devco coal employing a Ca/S molar ratio of 1.96. This low value was due to an unusually low bed temperature (768 deg. C). Information on superficial velocity for the US EPA tests is not available in the report [19]. However, any significant effect from the superficial velocity is unlikely since the data agree well with the statistic model.

For circulating FBC tests, the effect of superficial velocity was examined for the tests with Syncrude coke, Minto coal, CANMET pitch and the H-Oil pitch.

The sulphur capture observed in the tests with Syncrude coke was quite constant in the Ca/S molar ratio range 1.02 to 2.26 and velocities of 2.8-6.9 m/s, Fig. 7. This rules out any significant effect of superficial velocity. In the tests with CANMET pitch and Minto coal, the sulphur capture was found to increase slightly with superficial velocity as shown in Figs. 8 and 10. However, the tests with High-Oil pitch gave contrary results. The sulphur capture was found to be slightly higher at a superficial velocity of 6.4 m/s than at velocities between 8.2 and 8.8 m/s, Fig. 11. The limited amount and variation in the data makes it impossible to provide

clear evidence of a consistent effect of superficial velocity.

Theoretically, superficial velocity might affect sulphur capture in various ways. For example, residence time of SO_2 gas in the combustor decreases with increasing superficial velocity providing less time for reaction and removal of SO_2. Further, elutriation of limestone fines increases with increasing superficial velocity, leading to a decrease in reactivity of the in-bed limestone. These factors would be expected to reduce the efficiency of the sulphur capture. On the other hand, higher superficial velocities would improve the mixing in the bed and enhance the grinding effect on the limestone which would reduce the average size of the in-bed limestone and improve the reactivity of the limestone. However, one could expect to observe a significant effect of velocity only if a wide range of velocities were employed. Data available to us do not provide a sufficiently wide range of superficial velocity to indicate a major effect by superficial velocity.

4. ADDITIONAL ANALYSIS ON NO_x EMISSION

4.1 EFFECT OF VOLATILES CONTENT OF FUEL

Our examination indicates that NO_x emission is related to not only the nitrogen content of the fuel, but also to the fuel volatiles content. Figure 12 shows that the averaged conversion of fuel nitrogen to NO_x over the runs performed for each test program

increases slightly with the volatiles content of the fuel indicating that a larger portion of nitrogen in the coal volatiles is converted to NO_x than the nitrogen contained in char.

4.2 EFFECT OF SECONDARY TO PRIMARY AIR RATIO

Secondary to primary air ratio is an important parameter used to describe the operating conditions of a circulating FBC test. However, our analysis shows no observable effect of secondary to primary air ratio on the NO_x emission, Fig. 13. It appears that for the two circulating FBC's considered, the distance between the inlets for the secondary air and primary air is small compared to the total height of the combustor. Hence, the split of the air flow into primary and secondary air would not affect the fuel-N conversion process in the combustor.

4.3 CHEMICAL KINETICS OF NO_x FORMATION AND DESTRUCTION IN FLUIDIZED BED COMBUSTION

4.3.1 Johnsson Kinetic Model

The study of nitrogen chemistry in combustion has been pursued intensively for more than fifty years. At the present time, a number of reaction paths for formation and destruction of nitrogen species in combustion have been presented. The rate parameters for more than 250 elementary reactions have been summarized in a recent

survey [23]. A critical review is also provided by Jones et al [24]. Kinetic data directly required for modelling of formation and reduction of NO_x in fluidized bed combustion consist primarily of global reactions and heterogeneous reactions involving CaO and Char, particularly over the temperature range 700-950 deg. C. These data were not available until recently when studies on these reactions were carried out [25-35].

A kinetic model for NO_x production has been proposed recently by Johnsson [36, 37] based on a survey of the kinetic data for global and heterogeneous reactions. The model assumed that the fuel-N comprised char-N and volatile-N. The char-N was oxidized to NO during combustion. The volatile-N was assumed to be in the form of NH_3. The global reactions included for the formation and destruction of NO_x in fluidized bed combustion thus include:

$$NO + CO \xrightarrow{char} 1/2\ N_2 + CO_2 \qquad (4.1)$$

$$NO + CO \xrightarrow{CaO} 1/2\ N_2 + CO_2 \qquad (4.2)$$

$$NO + H_2 \xrightarrow{char} 1/2\ N_2 + H_2O \qquad (4.3)$$

$$NO + H_2 \xrightarrow{CaO} 1/2\ N_2 + H_2O \qquad (4.4)$$

$$NO + 2/3\ NH_3 \xrightarrow{CaSO_4} 5/6\ N_2 + H_2O \qquad (4.5)$$

$$NO + char \rightarrow 1/2\ N_2 + CO \qquad (4.6)$$

$$NO + 2/3\ NH_3 \rightarrow 5/6\ N_2 + H_2O \qquad (4.7)$$

$$NH_3 + 5/4\ O_2 \xrightarrow{CaO} NO + 3/2\ H_2O \qquad (4.8)$$

$$NH_3 + 5/4\ O_2 \xrightarrow{char} NO + 3/2\ H_2O \qquad (4.9)$$

$$NH_3 + 5/4\ O_2 \rightarrow NO + 3/2\ H_2O \quad (4.10)$$

$$2NH_3 \xrightarrow{CaO} N_2 + 3H_2 \quad (4.11)$$

$$2NH_3 + 3/2\ O_2 \xrightarrow{char} N_2 + 3H_2O \quad (4.12)$$

$$2NH_3 + 3/2\ O_2 \xrightarrow{CaO} N_2 + 3H_2O \quad (4.13)$$

At present, the literature provides information on the kinetics of only 4 of the 13 reactions, i.e., reactions (4.1), (4.2), (4.4) and (4.6). For the remaining reactions, the kinetic data used in the model were assumed or estimated from data where experiments were not designed to give kinetic information. The data were evaluated based on the criteria of reaction order, activation energy, temperature range and concentration level. Only reaction (4.2) meets all four criteria, five reactions, (4.1), (4.4), (4.6), (4.7) and (4.10), meet three and the remaining seven meet less than three criteria. It was therefore concluded in the survey that more information on the kinetics was needed before detailed modelling was possible [36, 37].

The relative importance of the reactions was evaluated by a single-phase plug-flow reactor model. The model considered only the nitrogen chemistry, however, it did not include reaction (4.3) for which kinetic data were not available. The calculation was based on assumed conditions including an exponentially decaying O_2 concentration and constant concentrations for CO and H_2. The release of NH_3 and NO from devolatilization and combustion of char were assumed to be proportional to the O_2 concentration. Despite

the simplicity of the model, these assumptions are considered to be reasonable and the results may be used for qualitative discussion.

The results suggest that heterogeneous reactions dominate the entire fuel-N conversion process. The accumulated conversion of fuel-N attributed to the homogeneous gas phase reactions was estimated as 0.012%. However, a more recent review suggested that for N_2O emission, homogeneous gas phase reactions may be more important than heterogeneous reactions [24].

4.3.2 Effects of Operating Parameters -- Comparison of Predictions with Experimental Data

In this model, it is believed that reduction of NO by CO and char is important. The model indicates that 27% of the volatiles-N, which is assumed to contribute 50% of the fuel-N and to be released as NH_3 in volatiles combustion, is oxidised to NO before being reduced to N_2 or emitted from the system. Considering that char-N is assumed to contribute 50% of the total fuel-N released as NO in char combustion, it may be concluded that 77% of the fuel-N is estimated to be converted to NO which is either reduced or emitted from the combustor.

The emission of NO is calculated to decrease by a factor of 10 with an increase in CO concentration from zero to 5000 ppm, clearly indicating the effect of CO on the NO emission. This is consistent with our observation that in general NO_x emission varied in the opposite direction to CO emission [1].

According to the model, O_2 concentration may affect NO_x emission through its effect on oxidation of NH_3 to NO. The calculation indicated a slight decrease in NO emission when oxidation was assumed to be first order compared to when it was assumed to be zero order. The increase in NO_x emission with increasing excess oxygen observed in many of the tests summarized in the previous report [1] is likely due to the effect of excess oxygen on CO concentration. However, the effect of excess oxygen on NO_x emission could be reversed if the effect of excess oxygen on the CO emission is reversed. Such a reversal effect was demonstrated by the tests conducted at the Summerside heating plant as mentioned in Section 5.8 in the previous report [1], where NO_x emission increased slightly with excess oxygen due to an increased CO concentration caused by enhanced elutriation of char fines.

According to the kinetic model, the effect of temperature on NO_x emission is largely due to reaction of NO with char, Eq. (4.6). As a result of the relatively large activation energy (E/R = 29700 K), the rate constant of this reaction is increased by a factor of three if the temperature is increased by 50 K. This explains the substantial increase in NO_x emission as bed temperature increases as reported for some of the tests summarized in the previous report [1]. Since the reduction of NO by CO is less temperature sensitive, the effect of temperature on the emission of NO_x is therefore expected to depend on the ratio between the amount of NO reduced by char to that reduced by CO.

Since CaO catalyzes both the formation and reduction of NO

through reactions (4.2), (4.4) and (4.8), NO_x emission may increase or decrease when limestone is added. These reactions account for the complex and somewhat inconsistent observations of NO_x emission in tests with limestone addition.

According to the kinetics, the effect of limestone addition would depend on operating conditions. NO_x emission would decrease on addition of CaO if the CO concentration is high since reaction (4.2) would be important. The model also predicts that the effect of CaO on fuel-N conversion would be influenced by the volatiles content of the fuel. When no volatiles are present, CaO acts only as a catalyst for NO reduction. Therefore, NO emission is likely to increase with limestone addition for a low volatiles fuel.

A similar relationship between CO concentration and volatiles content of the fuel was observed in tests with heavy oils, Fig. 14. Heavy oils usually contain a high volatiles content, e.g., 67.7% for H-Oil pitch, while similar levels are expected for CANMET pitch and #6 oil. The CO emission was low in tests with H-Oil pitch and CANMET pitch conducted at the UBC circulating FBC plant, ranging from 120 to 217 ppm. The NO_x emission was found to increase with Ca/S molar ratio, Fig. 14, due to the high volatiles content and the low CO concentration.

For tests with #6 oil conducted at the Mark II bubbling FBC plant, the NO_x emission did not vary with the Ca/S molar ratio unless a Ca/S molar ratio larger than 4 was employed, Fig. 14. For Ca/S molar ratios larger than 4, the NO_x emission increased with Ca/S molar ratio for those tests where CO emission was less than

284 ppm due to the low CO emission and high volatile content. However, the NO_x emission decreased with Ca/S molar ratio for those tests where CO emission ranged between 502 and 3127 ppm indicating that the effect of CO concentration outweighed the effect of volatiles content.

The NO_x emission observed in the tests with CANMET pitch conducted at the Mark II bubbling FBC unit decreased when limestone was added, Fig. 14. However, it is likely this decrease is caused by CO concentration rather than limestone addition. It is noted that the CO concentration observed in the two base line tests was much lower, 293-373 ppm, than that observed in the tests with limestone addition, 558-857 for three tests and 1242-2325 ppm for the remaining eight tests. As stated in the previous report, NO_x emission and CO emission usually vary in opposite directions.

There are still a number of observations of the effect of limestone which remain unexplained. A typical example is the tests with Syncrude coke, a fuel with volatiles content of 6.7%. The CO concentration was low in the tests conducted at the Pyroflow circulating FBC plant, less than 120 ppm with an exception of one datum at 650 ppm. Results were higher in the tests at the Queen's and the Mark II bubbling FBC plants, 1245-1925 ppm for three tests and 200-469 ppm for the remaining tests. However, the NO_x emission increased with limestone addition in the bubbling FBC tests and decreased in the tests at the Pyroflow circulating FBC tests as shown in Fig. 66 in the previous report.

A similar situation was found in the tests with Evans and

Minto coals, Figs. 63 and 65 in the previous report[1]. For the Evans coal tests, the CO emission ranged from 453 to 1007 ppm for the tests conducted at Summerside bubbling FBC heating plant and 176-598 ppm (with an exceptional datum at 6998 ppm) for the tests conducted at the Queen's bubbling FBC plant. However, the NO_x emission increased with limestone addition in the Summerside tests and decreased in the Queen's tests. For the Minto coal tests, the CO concentration was high in the tests conducted at the Queen's bubbling FBC unit, ranging from 1000 to 3700 ppm for 15 of the 18 tests. CO emission was low in the tests conducted at the UBC circulating FBC unit and the Mark I bubbling FBC unit, less than 260 ppm. However, an increase of NO_x emission with the limestone addition was observed in all the tests conducted in the three combustors.

It was noted that most of the unexplained observations of the effect of CaO on NO_x emission were related to bubbling FBC combustors. The formation and destruction of NO in the freeboard region is completely neglected in the kinetic model, which may be responsible for the inability to predict the complex effect of CaO on NO_x emission observed in the bubbling FBC systems.

4.4 COMPARISON OF NO_x EMISSION WITH REACTOR MODELS

Theoretically, almost every FBC-model could be used to predict the NO_x emission by incorporating kinetics describing formation and reduction of NO_x in the combustor. To date only a few reactor

models have been proposed for NO_x emission since kinetic data for global and heterogeneous reactions were not available until recent years. Models developed before these kinetic data were available have been neglected in this examination.

The single-phase plug-flow reactor model was proposed by Johnsson along with a kinetic model [36, 37] to evaluate the most recent kinetic information. As a reactor model, two major shortcomings are evident:

1) The model predicted that 6% of the fuel-N converted to NO, which is less than half of the averaged conversion level (13.8%) observed in the experiments.

2) The model was mainly designed for bubbling FBC systems. However, processes in the freeboard were neglected.

Another attempt to incorporate NO_x emission into an FBC-model was made by extending the DUT SURE model for bubbling FBC systems [38, 39]. As in the Johnsson model, processes in the freeboard were not considered. Moreover, only three reactions, (4.6), (4.8), and (4.12) were taken into account by this model. The authors believed that reduction of NO by C, H_2 and CO was only possible if there was no oxygen present. The reduction of NO to N_2 takes place primarily at the coal surface and Eq. (4.6) is the most important reduction reaction [40].

The model accurately predicted that NO_x emission increased with bed temperature, Ca/S molar ratio and air ratio (ratio of the amount of air fed to the stoichiometric amount). The model is not expected to explain the complexity in the effects of operating

parameters on NO_x emission due to the oversimplified kinetic model used. Since CO is completely omitted as a reactant from the kinetics, the generally observed effect of CO on NO_x emission remains unexplained.

The third model [41] available in the literature incorporates the Johnsson kinetic model into the plume model [42, 43]. Unfortunately, this model was aimed primarily at predicting the concentrations of NH_3 and NO_x in the bed. No predictions regarding effects of operating conditions on NO_x emission have been reported.

4.5 FURTHER DISCUSSION

The major difficulty encountered in theoretically reproducing NO_x emission data arises from the variation in effect of a specific operating parameter observed in different test programs. For example, the effect of bed temperature on NO_x emission shown in the UBC circulating FBC unit was not observed in the tests conducted at the Queen's bubbling FBC unit. This suggests that the kinetics of formation and destruction of NO_x varies unit to unit.

Our examination indicates two major mechanisms for reduction of NO exist under certain operating conditions. The first occurs when the concentration of CO in the combustor is low and char becomes the major reducing agent. Under these conditions, reactions (4.6), (4.8), (4.9), (4.12) and (4.13) are significant. For a qualitative analysis, reactions (4.9) and (4.13) may be neglected since CaO favours oxidation of NH_3 to NO while char favours

oxidation of NH_3 to N_2. In this manner, the kinetics of the formation and destruction of NO was greatly simplified as described by Van den Bleek et al [38, 39]. Since the reduction of NO by char is strongly temperature dependent, the NO_x emission is expected to increase with bed temperature. The NO_x emission is more likely to increase with limestone addition since CaO acts only as a catalyst for the formation of NO. Such an effect would be greater when a large Ca/S molar ratio is employed and the volatile content of the fuel is high. The excess air is also believed to have some positive effect on NO_x emission if the oxidation of NH_3 is assumed to be first order. However, such an effect is not expected to be large. As demonstrated by Johnsson [36, 37], the NO emission was calculated to vary only slightly when oxidation of NH_3 was assumed to be a zero order reaction rather than a first order reaction.

NO_x reduction by char is more likely to occur in circulating FBC systems. CO emission from circulating FBC systems is usually lower than that from bubbling FBC systems, due to a better mixing process in the combustor resulting in more oxygen being available to the burning coal particle. Also, the char particles generated in circulating FBC systems are much finer than in bubbling FBC systems. The char would still be the major reducing agent when heavy oils are used as fuel. Oil residues would deposit on the surface of bed particles to create a large carbon surface available for the reaction. A typical example is the tests conducted at the UBC circulating FBC plant. As shown in Figs. 40, 49 and 68, the NO_x emission observed in this plant increased with excess oxygen, bed

temperature and the addition of limestone. As mentioned in the previous report (page 50), the correlation between CO and NO_x emission was not observed in this plant.

When large fuel particles are used in a bubbling FBC system, the char surface available for the reaction may be significantly reduced. Under such circumstances, if the CO concentration in the combustor is high due to unsatisfactory mixing, another simplified scenario can be described in which CO dominates the reduction of NO. Since char plays an unimportant role, NO_x emission would be insensitive to variation in bed temperature. The emissions of CO and NO_x would vary in opposite directions in this situation: high NO_x emission is always related to low CO emission and vice versa. Since CO emission is often related to excess oxygen, higher NO_x emission is therefore expected when large excess oxygen is employed. Since CaO is expected to catalyze both the formation and reduction of NO in this situation, the effect of Ca/S molar ratio is expected to be complex and to depend on a number of operating conditions including the volatiles content of the fuel, the CO concentration and the amount of CaO available in the combustor. The condition of the freeboard would also be important due to the reduction of NO occurring in that region.

It should be emphasized that no model has yet considered the reactions in the freeboard.

The formation and reduction of NO in the tests conducted at the Summerside heating plant and the Queen's bubbling FBC plant may be considered as typical for the CO-reduction situation. No linkage

between bed temperature and NO_x emission was found in the tests conducted in these two plants. Instead, strong correlations between CO and NO_x emissions are evident, Figs. 60, 61 and 62. The CO emission can be related directly to the excess oxygen employed in the Queen's plant (see Fig. 70 in the previous report). The NO_x emission is therefore well correlated to the excess oxygen employed in that plant as shown in Figs. 38 and 39 in the previous report[1]. For the Summerside heating plant, the CO concentration increased slightly with excess oxygen due to freeboard combustion of elutriated char enhanced by the high velocity at high levels of excess oxygen (Fig. 70 in the previous report). The NO_x emission decreased slightly with the excess oxygen. No consistent trend was found in the tests conducted in these two plants in regard to the effect of Ca/S molar ratio on NO_x emission, substantiating the complex role played by CaO.

In more general cases, NO reduction by both char and CO are important and the situation may be considered as a mixture of these two extreme cases. Reduction by char and CO may weigh differently under different conditions. Therefore, a specific operating parameter may affect NO_x emission differently as summarized in the previous report[1].

5. CONCLUSION

5.1 SO_2 EMISSION

In addition to the sulphur content of the fuel, the emission of SO_2 observed in base line tests was found to be affected by the mineral content of the fuel. The sulphur capture increased with the equivalent Ca/S molar ratio calculated so as to include both the calcium and magnesium content of the fuel, following an empirical model derived from the tests with limestone addition. The model indicates that 69.3% of the fuel sulphur was emitted as gaseous SO_2. However, the SO_2 emission does not vary with the volatiles content of the fuel.

The results of the tests with limestone addition show that sulphur capture improved when small sized limestone was used. A recycle system returns limestone fines to the bed reducing the average size of the in-bed limestone and thereby enhancing the effect of limestone. However, no significant effect of limestone type has been observed.

Superficial velocity is expected to have both positive and negative effects on sulphur capture. As a result, the sulphur capture is found not to vary significantly with the superficial velocity in the range employed.

5.2 NO_x EMISSION

The NO_x emission is found to increase slightly with the volatiles content of the fuel. In circulating FBC tests, the NO_x emission does not vary with the secondary to primary air ratio, due, presumably, to the small distance between the inlets for the secondary air and the primary air compared to the height of the combustor.

The reaction paths for formation and destruction of NO in FBC combustors have been well established and a kinetic model has been proposed. The model provides a good kinetic background to explain qualitatively the general observation on variation of NO_x emission, such as increasing NO_x emission with decreasing CO concentration and increasing bed temperature. However, some of the effects of CaO on NO_x emission remain unexplained kinetically. Many key kinetic data are not available and more information is needed before detailed modelling for NO_x emission is possible.

At present, few reactor models have been developed to predict NO_x emission from fluidized bed combustion. The observations made on NO_x emission in the tests summarized in the previous report largely remain unexplained. Among the two most recent models, one was based on oversimplified kinetics without provision of the conditions for application. The second was designed for evaluation of the kinetic model itself and was based on oversimplified operating conditions.

Examination of NO_x emission and the kinetics of formation and destruction of NO indicates that two extreme situations may arise under certain conditions. (1) Reduction of NO by char, is more likely to be found in circulating FBC units. In this situation, the CO emission is low and no relationship between NO_x and CO emission exists. NO_x emission increases with bed temperature and may also increase with excess air. The NO_x emission also tends to increase with CaO addition especially when fuels with high volatiles content are used since CaO only acts as catalyst for NO formation in the low CO environment. The tests conducted at the UBC circulating FBC unit represent a typical example of such a situation. (2) Reduction of NO by CO, is more likely to be found in bubbling FBC systems. In this situation, the NO_x emission shows no relationship with bed temperature, but is strongly correlated to CO emission. High CO emission is always related to low NO_x emission. The NO_x emission is also related to excess air since high excess oxygen levels usually results in a low CO concentration. The effect of CaO on NO_x emission is complex since the CaO catalyzes both the formation and destruction of NO. The factors determining whether NO_x emission would increase or decrease with limestone addition include CO concentration level, volatile content of the fuel, and other operating conditions. The tests conducted at the Queen's bubbling FBC unit represent a typical example of this situation. In general cases, both the effects of CO and char are important but may weigh differently. Therefore the effect of a specific operating parameter may be different under different conditions.

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Table 1 Pilot BFBC tests with limestone addition

TEST NO.	LIMESTONE NAME	LIMESTONE SIZE mm	RECYCLE OR RECYCLE FRACTION*	SUPERFICIAL VELOCITY m/s
1. MINTO COAL TESTS AT QUEEN'S UNIV., QFBC. TR. 83.1 [2]:				
821116	HAVELOCK	0.78	1	1.59
830106	"	1.98	0.800	1.69
830112	"	0.78	0.963	1.68
830124	"	0.78	0.905	1.86
830126	"	0.78	0.836	1.75
830127	"	0.78	0.875	1.79
830201	"	0.78	0.919	1.86
830202	"	0.78	0.906	1.90
830215	"	0.78	0.600	2.77
830216	"	0.78	0.520	2.76
830217	"	0.78	0	2.70
830218	"	1.98	0	2.77
830224	"	1.72	0.570	2.68
830225	"	1.72	0.540	2.93
830226	"	1.72	0.610	2.87
830322	"	0.49	0	2.14
830324	"	0.49	0.700	2.06
830329	"	0.49	0.590	2.25
830330	"	0.49	0	2.02
2. MINTO COAL TESTS AT CCRL (MARK I), ERP/ERL 81-36(J) [11]:				
A1	HAVELOCK	1.1	NO	2.36
A2	"	1.1	NO	2.11
A3	"	1.1	NO	2.36
A4	"	1.1	NO	2.08
A5	"	1.1	NO	2.20
A6	"	1.1	NO	2.23
6. DEVCO COAL TESTS AT QUEEN'S UNIV., QFBC. TR. 83.1 [2]:				
830309	HAVELOCK	1.72	0.857	1.90
830310	"	1.72	0.760	1.90
830315	"	1.72	0.700	2.73
830316	"	1.72	0.760	2.67

* Fraction of cycloned dust that is returned to combustor.

Table 1 Pilot BFBC tests with limestone addition (cont.)

TEST NO.	LIMESTONE NAME	LIMESTONE SIZE mm	RECYCLE OR RECYCLE FRACTION*	SUPERFICIAL VELOCITY m/s
7. DEVCO COAL TESTS AT QUEEN'S UNIV., QFBC. TR. 85.1 [3]:				
841127	SYSCO	1.4	0	2.5
841204	"	1.4	0.691	2.5
841218	CALPO	1.1	0	2.5
841219	"	1.1	0.775	2.5
850107	"	1.1	0	1.5
850115	"	1.1	0	1.5
850129	SYSCO	1.4	0	2.4
850304	"	1.4	0	1.5
8. DEVCO COAL TESTS AT CCRL (MARK II), ERP/ERL 85-44 (OPJ) [13]:				
DC1	HAVELOCK	0-6.3	NO	3.0
DC2	"	0-6.3	YES	3.0
DC3	"	0-6.3	NO	2.1
DC4	"	0-6.3	YES	2.1
DC5	"	0-6.3	NO	1.2
DC6	"	0-6.3	YES	1.2
DC7	"	0.84-2.38	NO	3.0
DC8	"	0.84-2.38	YES	3.0
DC9	"	0.84-2.38	NO	2.1
DC10	"	0.84-2.38	YES	2.1
DC11	"	0.84-2.38	NO	1.2
DC12	"	0.84-2.38	YES	1.2
DC14	"	0.84-6.3	YES	3.0
DC15	"	0.84-6.3	NO	2.1
DC16	"	0.84-6.3	YES	2.1
DC17	"	0.84-6.3	NO	1.2
DC18	"	0.84-6.3	YES	1.2
DC20	"	0-6.3	YES	2.1
DC21	"	0.84-2.38	NO	2.1
DC22	"	0.84-2.38	YES	2.1
DC23	"	0.84-6.3	NO	2.1
DC24	"	0.84-6.3	YES	2.1
DC25	"	0.1	NO	2.1
DC26	"	0.1	YES	2.1
DC27	"	0.4	NO	2.1
DC28	"	0.4	YES	2.1
EDC1A	"	0-6.3	YES	2.1
EDC1B	"	0-6.3	YES	1.2
EDC1C	"	0-6.3	YES	2.1
EDC2A	"	0.84-2.38	YES	2.1
EDC2B	"	0.84-2.38	YES	1.2

Table 1 Pilot BFBC tests with limestone addition (cont.)

TEST NO.	LIMESTONE NAME	LIMESTONE SIZE mm	RECYCLE OR RECYCLE FRACTION*	SUPERFICIAL VELOCITY m/s
10. EVANS COAL TESTS AT QUEEN'S UNIV., QFBC. TR. 85.1 [3]:				
831115	HAVELOCK	0.49	0	2.1
831122	"	0.49	0	2.1
831124	"	0.49	0.555	2.2
831213	"	1.72	0	2.5
831214	"	1.72	0.607	2.6
840105	"	1.72	0.965	2.6
840111	"	1.72	0.924	2.0
840117	"	1.72	0.945	1.5
840124	"	0.49	0.963	1.5
840126	"	0.49	0	1.6
840207	"	0.49	0	2.1
840215	"	0.49	0.555	2.3
840216	"	0.49	0	2.2
840313	"	0.49	1	1.5
840314	"	0.49	0	1.6
840320	"	0.49	0	1.5
15. WESTERN KENTUCKY NO.9 COAL TESTS AT QUEEN'S UNIV. QFBC. TR. 85.1 [2]:				
841108	REED	1.1	0	2.6
841112	"	1.1	0	2.7
841115	"	1.1	0	2.6
841119	"	1.1	0.636	2.9
24. ONAKAWANA LIGNITE TEST AT CCRL (MARK I), ERP/ERL 81-30 (CF) [9]:				
8	HAVELOCK	0-6	NO	2.59
25. ONAKAWANA LIGNITE TESTS AT CCRL MARK (II), ERP/ERL 87-67 (OPJ) [16]:				
5	HAVELOCK	0-6	NO	2.13
6	"	0-6	YES	2.13
7	"	0-6	NO	2.13

Table 1 Pilot BFBC tests with limestone addition (cont.)

TEST NO.	LIMESTONE NAME	LIMESTONE SIZE mm	RECYCLE OR RECYCLE FRACTION*	SUPERFICIAL VELOCITY m/s
27. WASHERY REJECT TESTS AT CCRL (MARK II), ERP/ERL 87-71 [17]:				
PR1	HAVELOCK	0-6.3	NO	1.26
PR2	"	0-6.3	YES	1.33
PR3	"	0-6.3	YES	2.40
PR4	"	0-6.3	YES	2.39
PR5	"	0-6.3	YES	2.45
PR5A	"	0-6.3	YES	1.84
PR6	"	0-6.3	NO	2.33
PR7	"	0-6.3	YES	1.83
PR8	"	0-6.3	YES	1.78
PR9	"	0-6.3	NO	1.56
28. SYNCRUDE COKE TESTS AT QUEEN'S UNIV. QFBC. TR. 85.1 [3]:				
840605	HAVELOCK	0.3	0	0.9
840612	ATHABASCA	0.34	0	1.3
840618	"	0.34	0	1.0
840703	"	0.34	0.69	1.0
840731	"	0.94	0.83	1.1
840814	"	0.94	0.69	0.8
840820	"	0.94	0.81	0.8
840827	"	0.94	0.83	0.9
840911	"	0.94	0.75	1.1
29. SYNCRUDE COKE TESTS AT CCRL (MARK II), ERP/ERL 86-74 (TR) [14]:				
SC1	ATHABASCA	0-6	NO	0.85
SC2	"	0-1.7	NO	0.76
SC3	"	0-1.7	YES	0.74
SC4	"	0-1.7	YES	0.93
31. SUNCOR COKE TESTS AT CCRL (MARK I), ERP/ERL 81-27 (TR) [7]:				
23	HAVELOCK	0-6	NO	2.51
32. SASKATCHEWAN PETROLEUM COKE TESTS AT QUEEN'S UNIV., QFBC. TR. 87.5 [5]:				
860317	ATHABASCA	0.83	0.633	1.90
860318	"	0.83	0.963	1.69
860324	"	0.83	0.951	1.91

Table 1 Pilot BFBC tests with limestone addition (cont.)

TEST NO.	LIMESTONE NAME	LIMESTONE SIZE mm	RECYCLE OR RECYCLE FRACTION*	SUPERFICIAL VELOCITY m/s
33. COAL/WATER SLURRY TESTS AT QUEEN'S UNIV., QFBC. TR. 87.6 [6]:				
870713	HAVELOCK	0.49	0	1.66
870714	"	0.49	0.89	1.67
870723	"	0.49	0	2.23
34. NO.6 OIL TESTS AT CCRL (MARK II) ERP/ERL 87-22 (CF) [14]:				
OIL05	HAVELOCK	0.85-2.36	YES	2.0
OIL06	"	0.85-2.36	YES	2.0
OIL09	"	0.85-2.36	YES	2.1
OIL10	"	0.85-2.36	YES	2.1
OIL11	"	0.85-2.36	YES	1.9
OIL12	"	0.85-2.36	YES	1.9
OIL13	"	0.85-2.36	YES	2.1
OIL14	"	0.85-2.36	YES	2.0
OIL17	"	0.85-2.36	NO	1.3
OIL18	"	0.85-2.36	NO	1.4
OIL19	"	0.85-2.36	YES	1.4
OIL20	"	0.85-2.36	YES	1.3
OIL21	"	0.85-2.36	YES	2.0
OIL22	"	0.85-2.36	YES	2.1
35. CANMET PITCH TESTS AT CCRL (MARK II), ERP/ERL 87-22 (CF) [14]:				
CP2	ATHABASCA	0-6.4	YES	2.0
CP2A	"	0-6.4	YES	2.0
CP2B	"	0-6.4	YES	2.0
CP2C	"	0-6.4	YES	2.0
CP2D	"	0-6.4	YES	2.0
CP9	HAVELOCK	0.85-2.36	YES	2.0
CP9A	"	0.85-2.36	YES	2.1
CP9C	"	0.85-2.36	YES	2.1
CP9D	"	0.85-2.36	YES	2.2
CP9E	"	0.85-2.36	YES	2.2
CP7	"	0.85-2.36	YES	2.8
40. BITUMEN TESTS AT CCRL (MARK II), ERP/ERL 87-22 (CF) [14]:				
BIT1	HAVELOCK	0.85-2.36	YES	1.4
BIT2	"	0.85-2.36	YES	1.7
BIT4	"	0.85-2.36	YES	1.9

Table 2 Information on Summerside tests

TEST NO.	LIMESTONE NAME	LIMESTONE SIZE mm	Ca/S RATIO	SUPERFICIAL VELOCITY m/s
3. MINTO COAL TESTS AT SUMMERSIDE HEATING PLANT [18]:				
100% MCR	HAVELOCK	0.85-2.36	2.39	3.44
65% MCR	"	"	1.98	4.66
23% MCR	"	"	1.62	2.61
9. DEVCO COAL TESTS AT SUMMERSIDE HEATING PLANT [18]:				
100% MCR	HAVELOCK	0.85-2.36	2.06	3.52
65% MCR	"	"	3.04	2.00
23% MCR	"	"	1.96	
11. EVANS COAL TESTS AT SUMMERSIDE HEATING PLANT [18]:				
100% MCR	HAVELOCK	0.85-2.36	3.05	4.57
65% MCR	"	"	2.62	3.44
23% MCR	"	"	1.37	3.20
12. EVANS COAL TESTS AT SUMMERSIDE HEATING PLANT, U.S. EPA TESTS [19]:				
FULL LD.	HAVELOCK	0.85-2.36	3.7	
PART LD.	"	0-6.3	4.5	
MAX. S. CAPT.	"	0.85-2.36	7.2	
13. BROGAN COAL TESTS AT SUMMERSIDE HEATING PLANT [18]:				
100% MCR	HAVELOCK	0.85-2.36	2.52	3.54
65% MCR	"	"	2.62	2.40
23% MCR	"	"	1.92	2.75
14. NOVACO COAL TESTS AT SUMMERSIDE HEATING PLANT [18]:				
100% MCR	HAVELOCK	0.85-2.36	1.91	3.03
65% MCR	"	"	1.35	4.60
23% MCR	"	"	0.68	2.83

Table 3 Information on pilot circulating FBC tests

TEST NO.	LIMESTONE NAME	LIMESTONE SIZE mm	Ca/S RATIO	SUPERFICIAL VELOCITY m/s	SECONDARY TO PRIMARY AIR RATIO
4. MINTO COAL TESTS IN CFBC AT UBC, CONTRACT 24ST 23440-6-9007 [19]:					
1	ELMTREE	0.21	1.36	7.0	1.0
2	"	0.21	1.36	8.1	1.5
3	"	0.21	1.36	7.9	1.4
4	"	0.21	1.36	7.6	0.4
5	"	0.21	1.36	9.8	1.5
6	"	0.21	1.36	10.8	1.4
7	"	0.21	1.63	7.1	1.1
8	"	0.21	2.17	6.8	1.1
9	"	0.21	2.72	7.9	1.1
5. MINTO COAL TESTS IN CFBC AT UBC, CONTRACT 52SS 23440-7-9136 [22]:					
RUN3-C1	24% ELMTREE 76% TEXLIME	0.21	3.0	8.4	1.22
RUN16-1	HAVELOCK	0.21	3.0	8.6	0.96
RUN16-2	"	0.21	3.0	8.7	1.91
RUN16-3	"	0.21	1.8	8.7	1.91
RUN16-4	"	0.21	1.8	8.8	0.96
RUN16-5	"	0.21	1.8	7.7	1.07
RUN16-6	"	0.21	3.0	7.8	1.07
20. HIGHVALE COAL TESTS IN CFBC AT UBC, CONTRACT 52SS. 23440-7-9136 [22]:					
RUN9-1			0	6.5	0.83
RUN9-2			0	7.0	1.89
RUN10-1			0	6.6	0.71
RUN10-2			0	6.8	1.84
RUN11-1			0	8.1	1.11
RUN11-2			0	9.3	1.99
RUN12-1			0	8.1	1.11
RUN12-2			0	9.5	1.89
23. MT KLAPPAN COAL TESTS IN CFBC AT UBC, CONTRACT 52SS. 23440-7-9136 [22]:					
RUN14-1			0	7.7	1.0
RUN14-2			0	7.8	0.5
RUN14-3			0	7.9	2.0
RUN14-4			0	6.0	2.0
RUN14-5			0	6.2	1.0
RUN7-1			0	7.8	1.0

Table 3 Information on pilot circulating FBC tests (cont.)

TEST NO.	LIMESTONE NAME	LIMESTONE SIZE mm	Ca/S RATIO	SUPERFICIAL VELOCITY m/s	SECONDARY TO PRIMARY AIR RATIO
26. POPLAR RIVER LIGNITE TESTS IN CFBC AT UBC, CONTRACT 52SS. 23440-7-9136 [22]:					
RUN15-1			0	8.4	1.07
RUN15-2			0	8.8	2.03
RUN15-3			0	6.9	1.28
RUN15-4			0	8.6	2.00
30. SYNCRUDE COKE TESTS IN CFBC AT KARHULA, FINLAND [21]:					
4	GOTLAND	0.315	2.04	6.1	0.65
5	"	0.315	1.54	5.6	0.59
6	"	0.315	2.26	5.3	0.69
7A	"	0.315	2.11	4.6	0.59
8A	"	0.315	1.71	5.3	0.59
7B	"	0.315	1.64	5.3	0.62
8B	"	0.315	1.65	5.6	0.61
9	"	0.315	1.72	5.8	0.61
10	"	0.315	1.73	6.3	0.61
11	"	0.315	1.76	6.9	0.61
12	"	0.315	1.34	4.0	0.70
13	"	0.315	1.41	3.8	0.67
14	"	0.315	1.21	3.1	0.93
15	"	0.315	1.03	2.8	0.93
16	"	0.315	1.53	5.5	0.61
36. CANMET PITCH TESTS IN CFBC AT UBC, CONTRACT 24St. 23440-6-9007 [19]:					
1	TEXLIME	0.214	1.7	7.5	0.56
2	"	0.214	1.5	7.8	1.07
3	"	0.214	2.3	7.5	1.05
4	"	0.214	2.3	5.6	1.03
37. CANMET PITCH TESTS IN CFBC AT UBC, CONTRACT 52SS. 23440-7-9136 [22]:					
RUN17-1	TEXLIME	0.214	2.5	8.8	0.80
RUN17-2	"	0.214	2.5	8.3	1.77
RUN17-4	"	0.214	1.3	8.4	0.85
RUN17-5	"	0.214	3.9	8.5	0.86
RUN17-6	"	0.214	3.9	8.3	1.87

Table 3 Information on pilot circulating FBC tests (cont.)

TEST NO.	LIMESTONE NAME	LIMESTONE SIZE mm	Ca/S RATIO	SUPERFICIAL VELOCITY m/s	SECONDARY TO PRIMARY AIR RATIO
38. H-OIL PITCH TESTS IN CFBC AT UBC, CONTRACT 24St.23440-6-9007 [19]:					
1	TEXLIME	0.214	0.54	7.0	0.52
2	"	0.214	0.68	7.8	0.57
3	"	0.214	1.20	8.2	0.58
39. H-OIL PITCH TESTS IN CFBC AT UBC, CONTRACT 52SS. 23440-7-9136 [22]:					
RUN18-BL	TEXLIME	0.214	0	9.2	0.70
RUN18-C1	"	0.214	3.5	6.4	0.32
RUN20-BL	"	0.214	0	7.5	0.82
RUN20-2	"	0.214	2.6	8.2	0.81
RUN20-3	"	0.214	5.6	8.5	0.77
RUN20-4	"	0.214	4.5	8.8	0.80

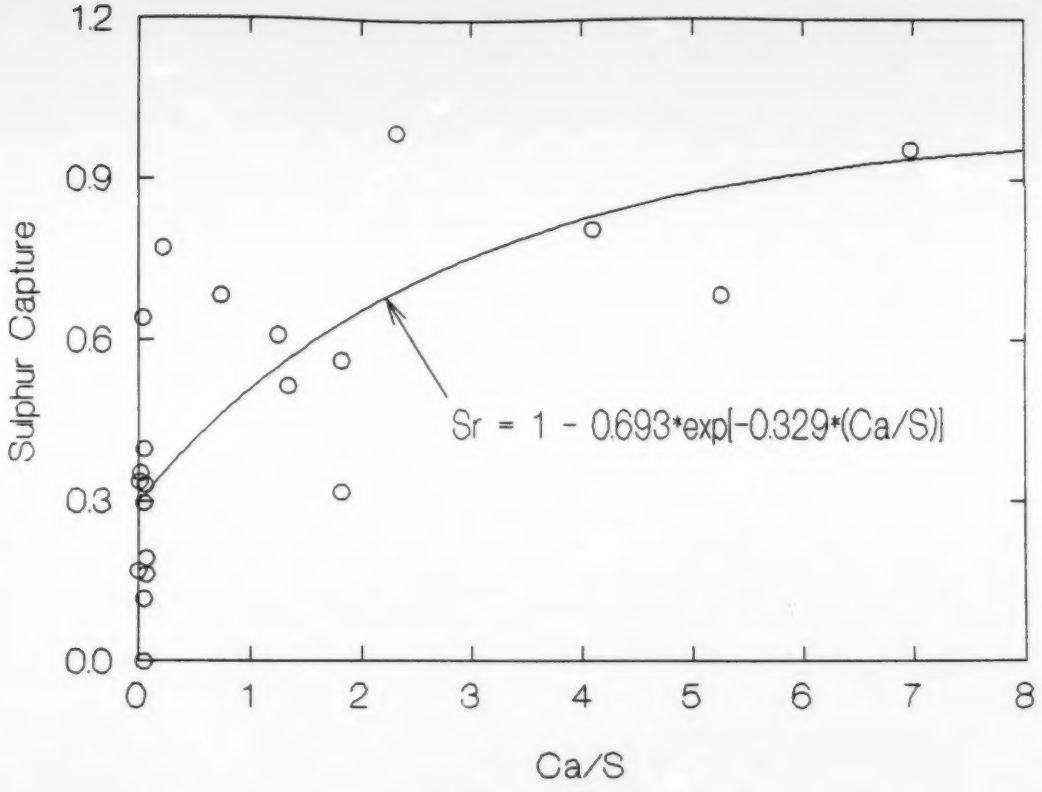

Fig. 1 Effect of fuel Ca/S molar ratio on sulphur capture in base line tests (no addition of sorbent). Sr is the fraction of fuel sulphur retained.

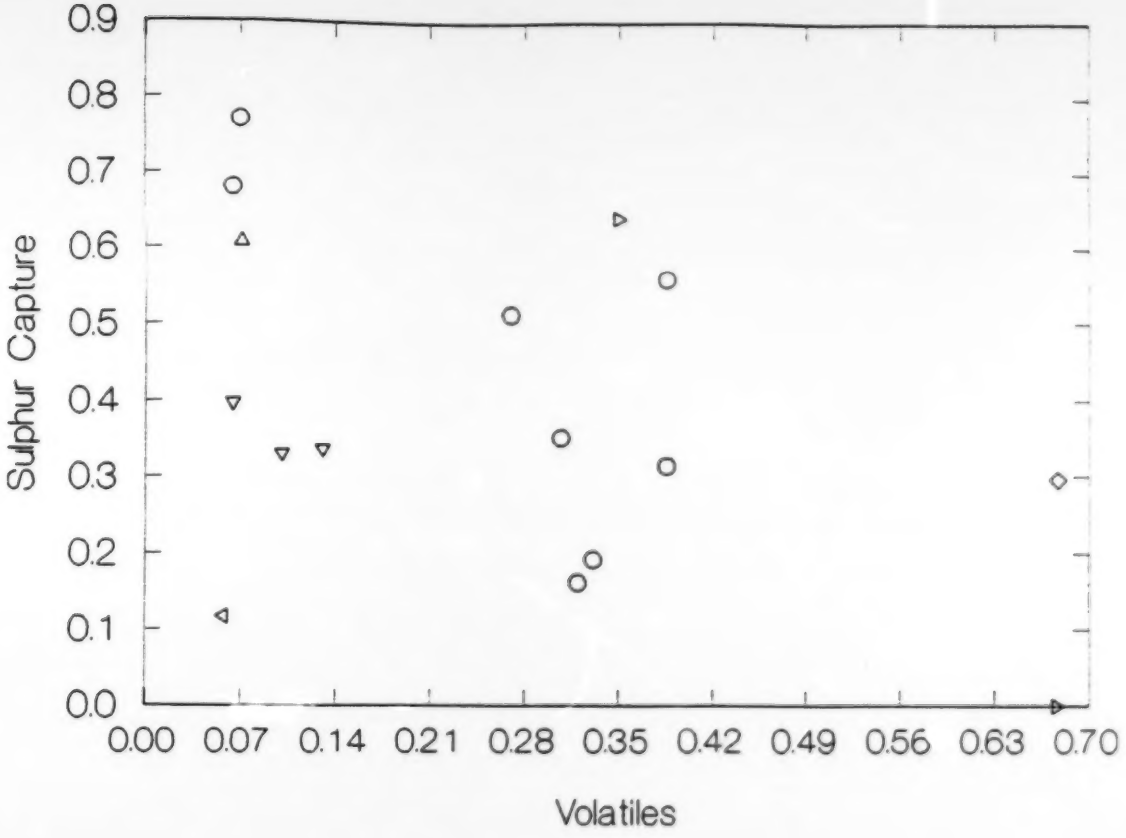

Fig. 2 Effect of volatiles content of fuel on sulphur capture in base line tests (no addition of sorbent).

Legend:
- ○ coal, bubbling FBC
- △ coal circulating FBC
- ▽ petroleum coke, bubbling FBC
- ◁ petroleum coke, circulating FBC
- ▷ liquid fuel, bubbling FBC
- ◇ liquid fuel, circulating FBC

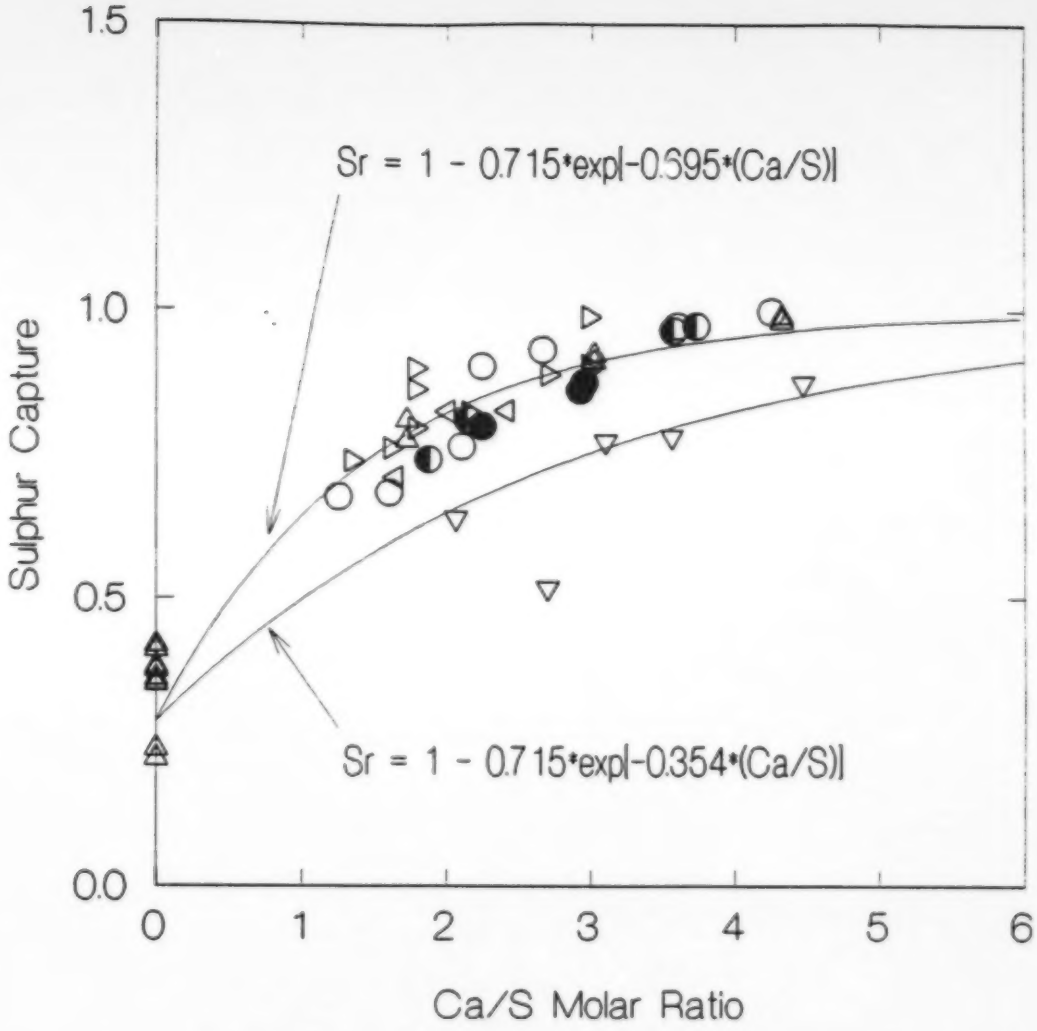

Fig. 3 Effect of Ca/S molar ratio on sulphur capture of Minto coal.

Facility, limestone size and superficial velocity:

- ○ Queen's Univ. bubbling FBC, 0.49-0.78 mm, 1.6-1.9 m/s
- ◐ Queen's Univ. bubbling FBC, 0.49-0.78 mm, 2.0-2.3 m/s
- ● Queen's Univ. bubbling FBC, 0.49-0.78 mm, 2.7-2.8 m/s
- ▽ Queen's Univ. bubbling FBC, 1.72-1.98 mm
- △ Mark I bubbling FBC, 1.1 mm
- ◁ Summerside heating plant, 0.85-2.36 mm
- ▷ UBC circulating FBC, 0.21-0.45 mm

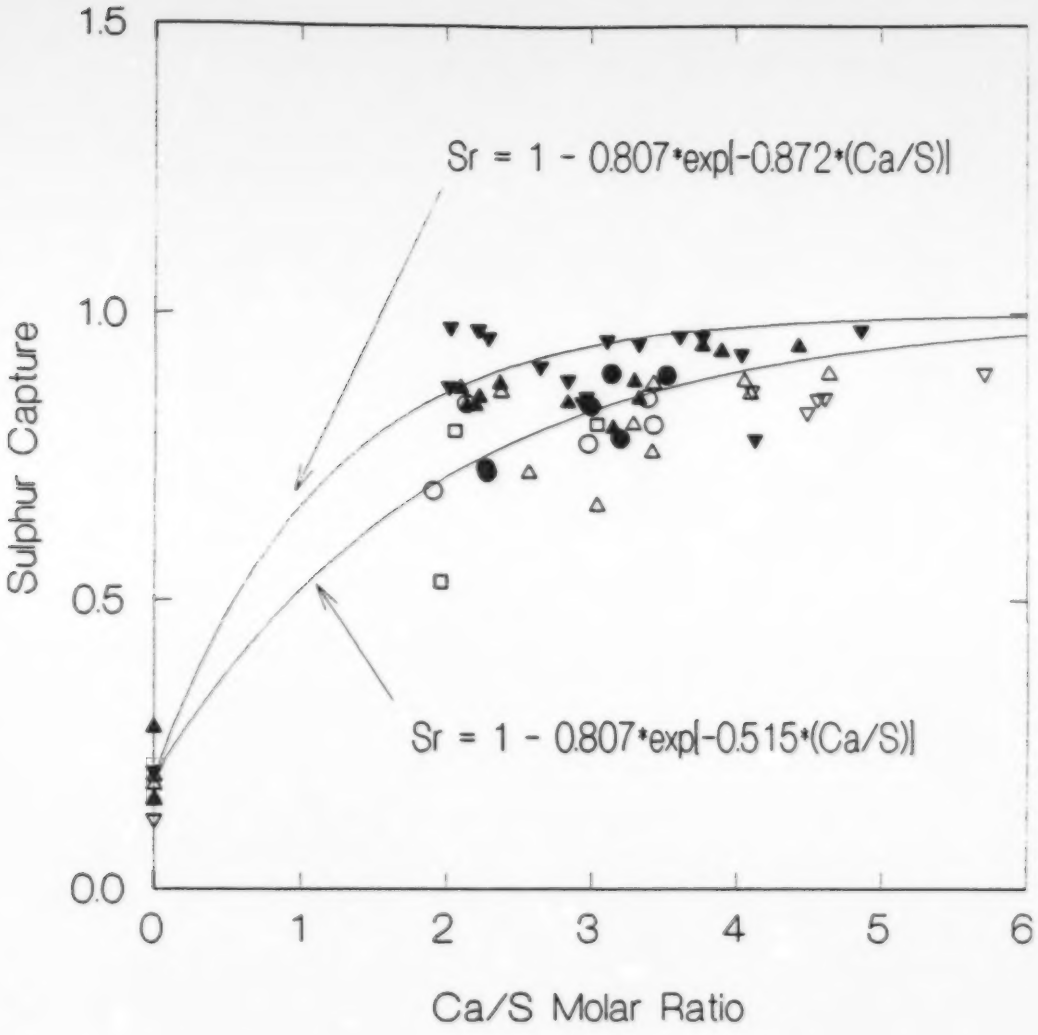

Fig. 4 Effect of Ca/S molar ratio on sulphur capture of Devco coal.

Legend: ○ **Queen's Univ. bubbling FBC, limestone size 1.1-1.72 mm**
△ **Mark II bubbling FBC, limestone size 0.84-6 mm**
▽ **Mark II bubbling FBC, limestone size 0-6.3 mm**
□ **Summerside heating plant**
Filled symbols, with recycle; open symbols, without recycle.

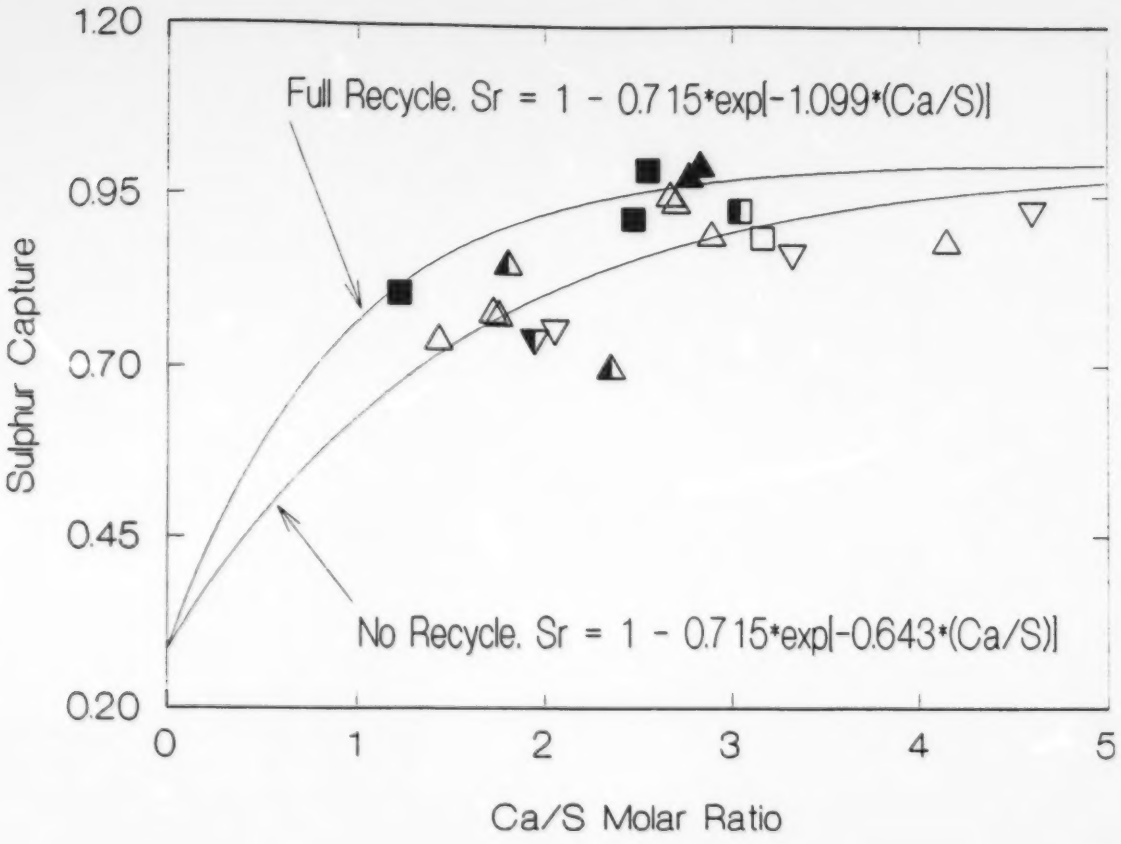

Fig. 5 Effect of Ca/S molar ratio on sulphur capture of Evans and Kentucky NO. 9 coals observed at Queen's Univ. bubbling FBC pilot plant.

Legend: □ **Evans, limestone size 1.72 mm**
△ **Evans, limestone size 0.49 mm**
▽ **Kentucky NO. 9, limestone size 1.1 mm**
Filled symbols, recycle fraction 0.92-1.0; half filled symbols, recycle fraction 0.56-0.64; open symbols, without recycle.

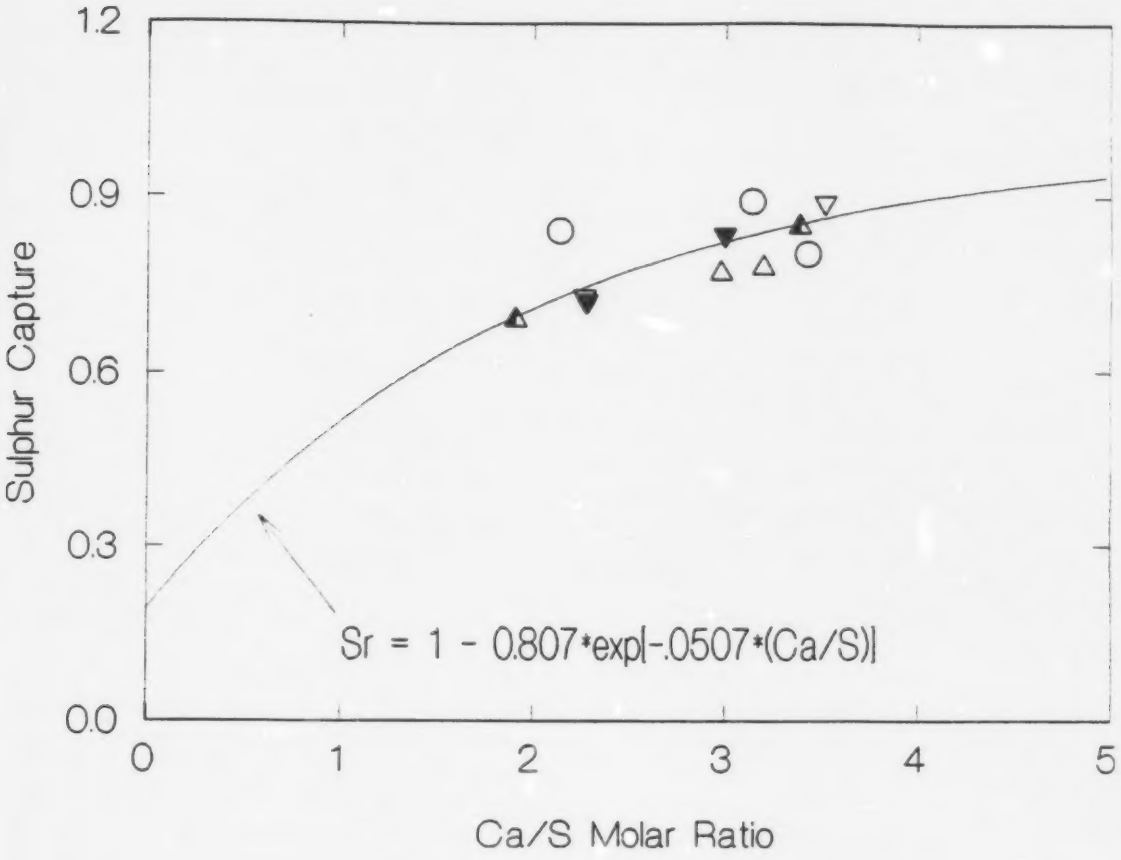

Fig. 6 Effect of limestone type on sulphur capture observed in tests with Devco coal conducted at Queen's University

legend: ▽ Havelock limestone, 1.72 mm, Ca/S = 2.3-3.5
○ Sysco limestone, 1.4 mm, Ca/S =2.1-3.4
△ Calpo limestone, 1.1 mm, Ca/S = 1.9-3.4
Filled symbols, superficail velocity = 1.9 m/s; half filled symbols, superficial velocity = 1.5 m/s; open symbols, superficial velocity = 2.4-2.7 m/s.

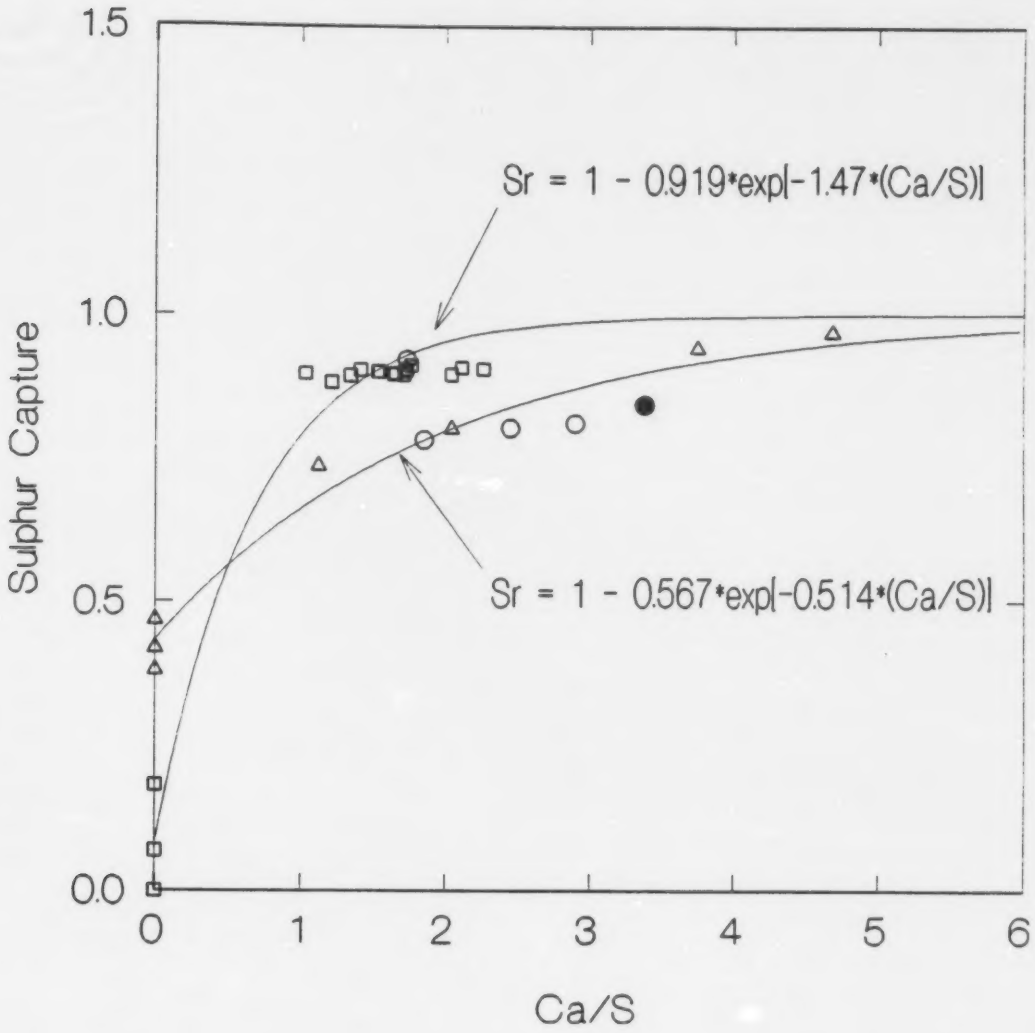

Fig. 7 Effect of Ca/S molar ratio on sulphur capture of Syncrude coke. Results for bed temperature above 1050 deg. C are excluded.

Legend:

- ○ Queen's Univ. bubbling FBC, filled symbol, Havelock limestone, 0.3 mm; open symbols, Athabasca limestone, 0.34 and 0.94 mm
- △ Mark II bubbling FBC, Athabasca limestone, 0-6 mm
- □ circulating FBC in Finland, Gotland limestone, 0.315 mm

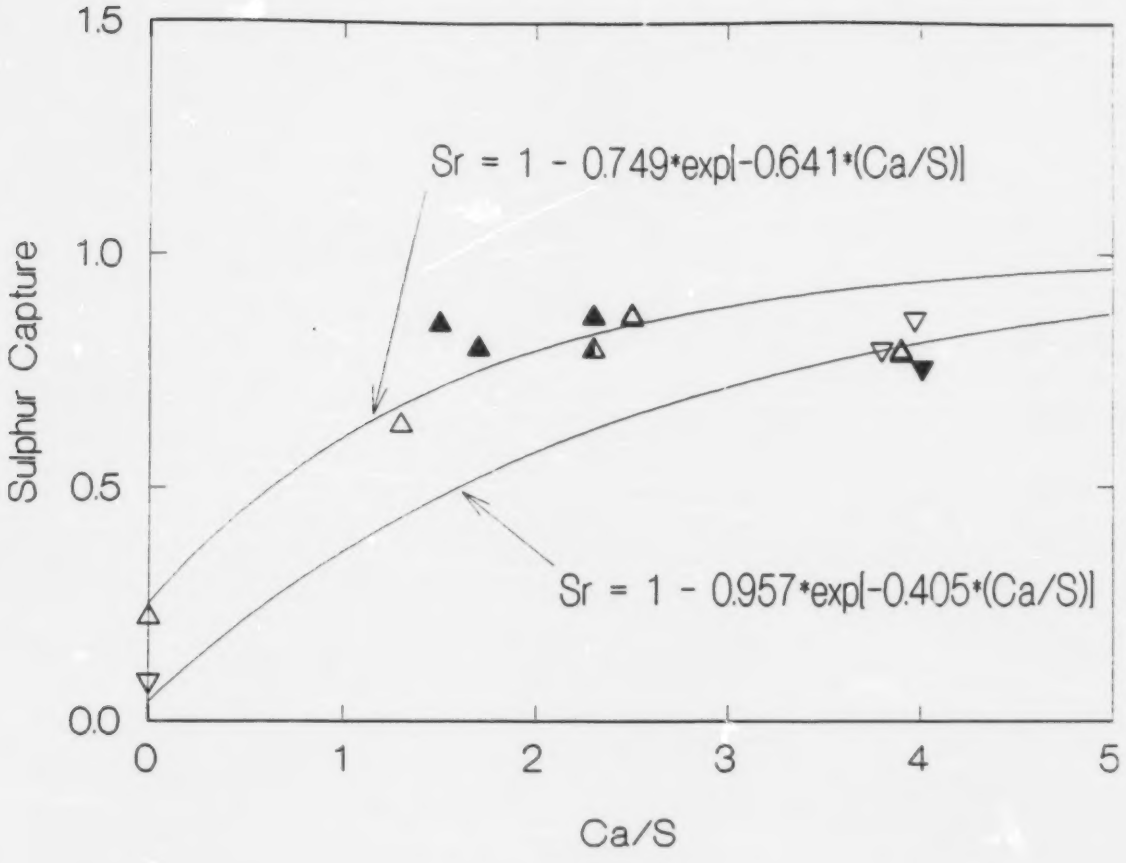

Fig. 8 Variation of sulphur capture with Ca/S molar ratio and the effect of limestone type and superficial velocity observed in tests with CANMET pitch.

Legend: ▽ Mark II bubbling FBC; filled symbol, Athabasca limestone, 0-6.4 mm; open symbols, Havelock limestone, 0.85-2.36 mm

△ UBC circulating FBC, Texlime limestone; 0.214 mm, filled symbols, velocity = 7.5-7.8 m/s; half filled symbol, velocity = 5.6 m/s; open symbols, velocity = 8.3-8.8 m/s

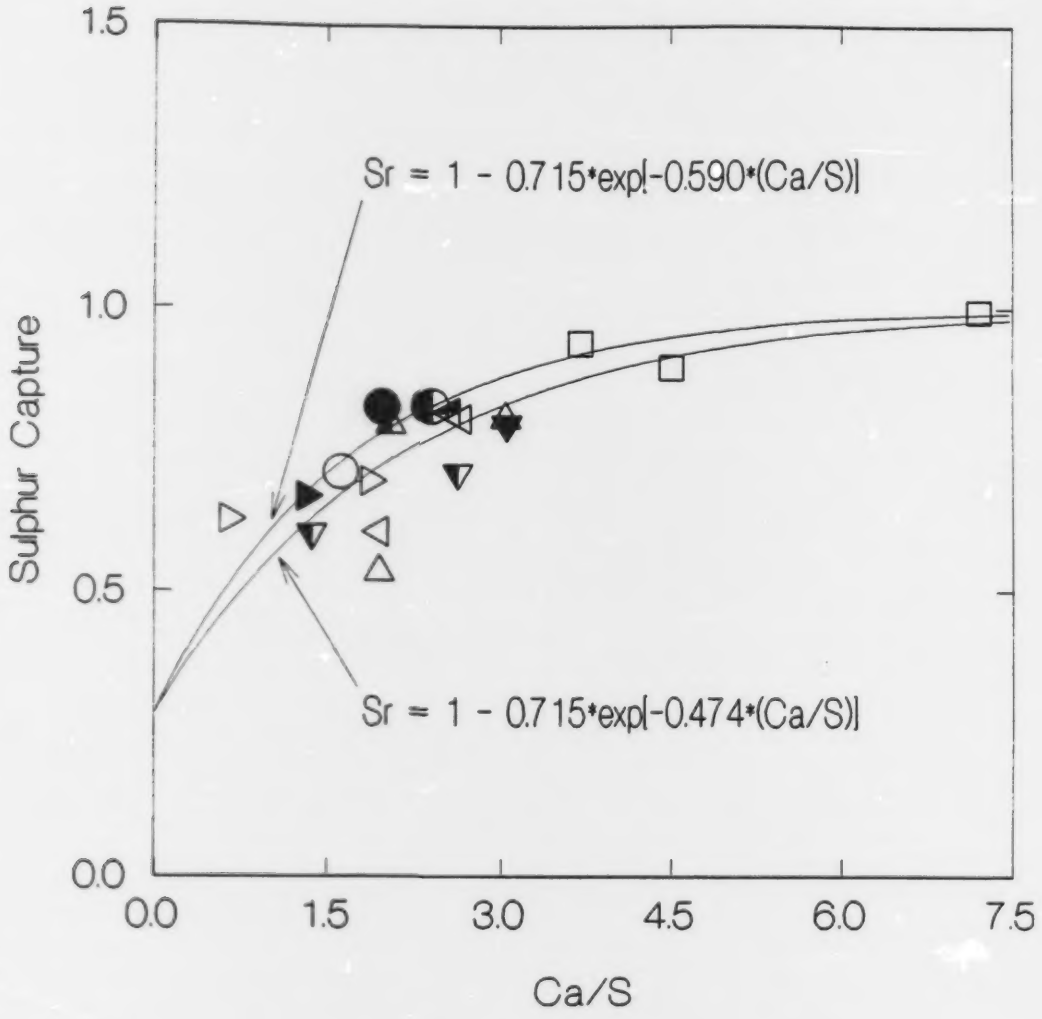

Fig. 9 Effect of Ca/S molar ratio on sulphur capture observed at the Summerside heating plant.

Coal:

▽	Evans, CANMET tests	□	Evans, US EPA tests
○	Minto	△	Devco
◁	Brogan	▷	Novaco

Open symbols, velocity = 2.0-3.0 m/s; half filled symbols, velocity = 3.2-3.5 m/s; filled symbols, velocity = 4.6-4.7 m/s.

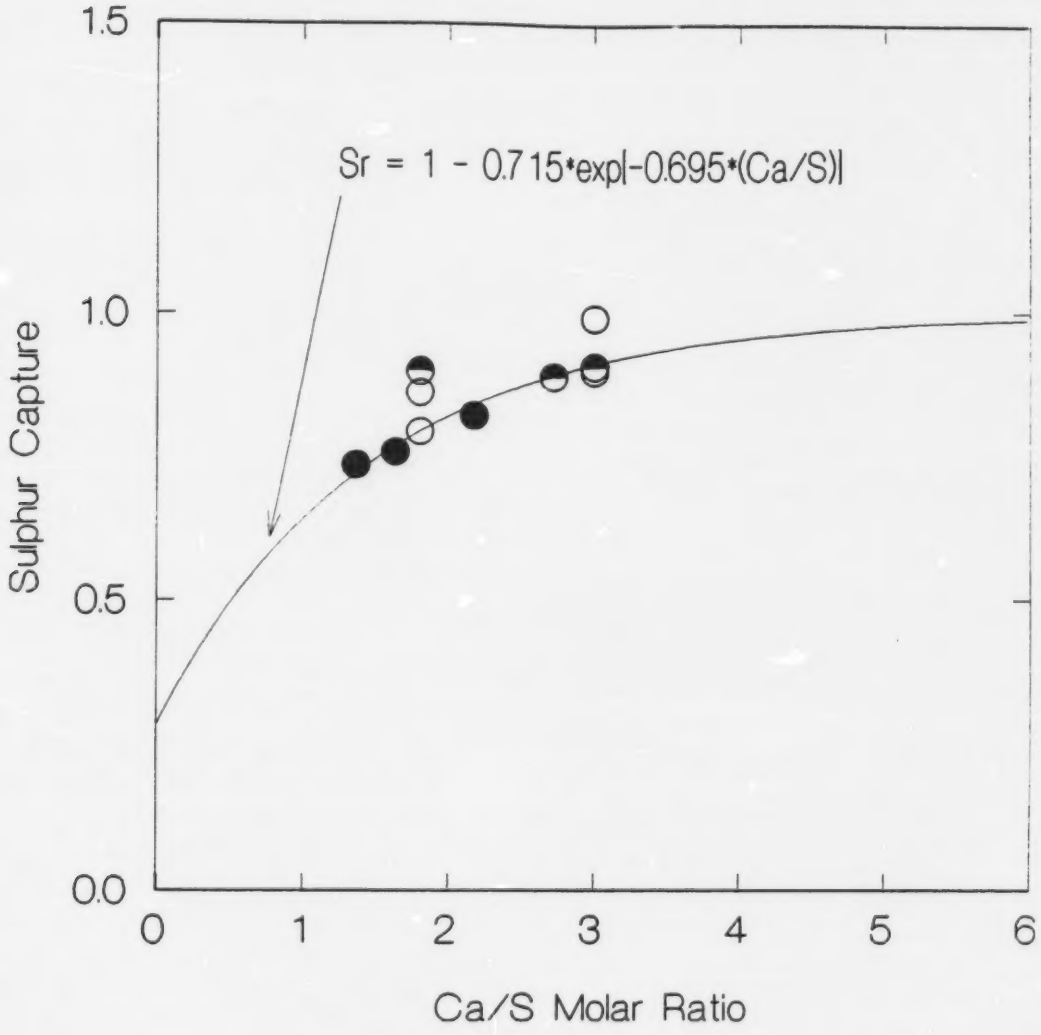

Fig. 10 Effects of Ca/S molar ratio and superficial velocity on sulphur capture observed in circulating FBC tests with Minto coal conducted at UBC. Filled symbols, velocity = 6.8-7.1 m/s; half filled symbols, velocity = 7.7-7.9 m/s; open symbols, velocity = 8.4-8.8 m/s.

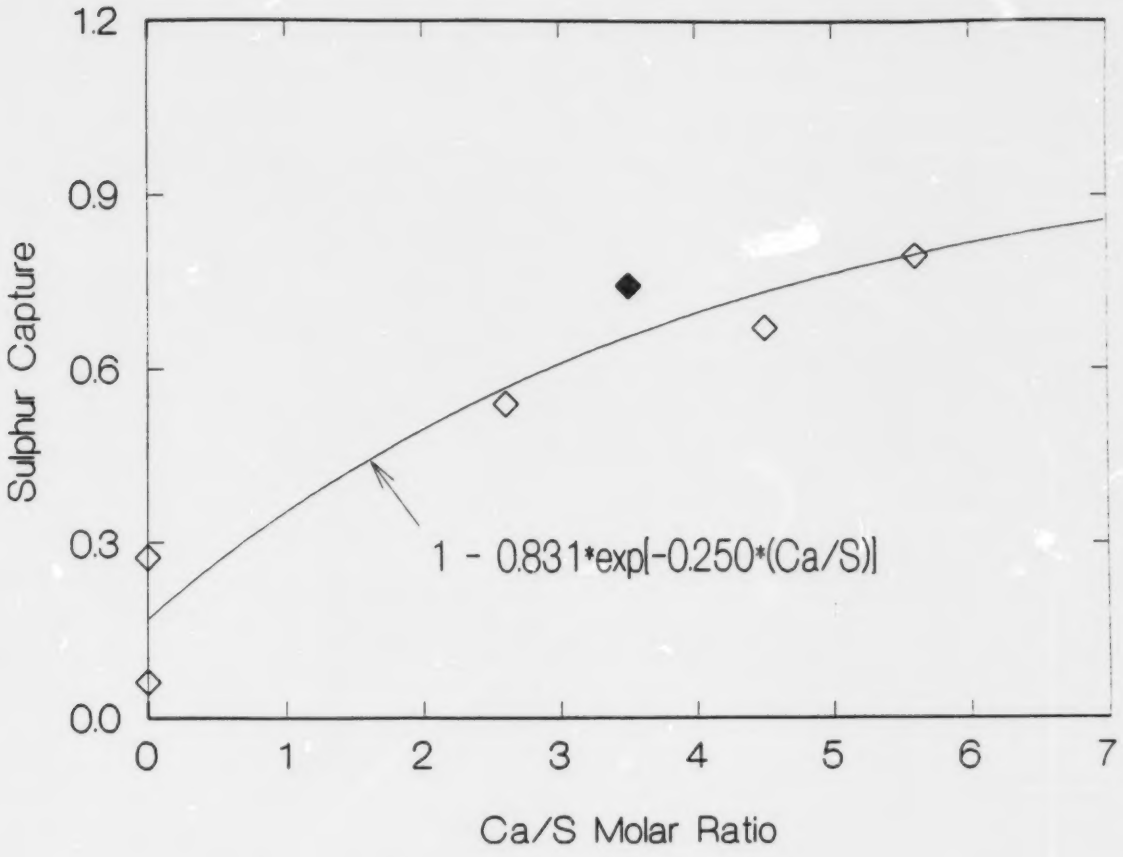

Fig. 11 Variation of sulphur capture with Ca/S molar ratio and the effect of superficial velocity observed in circulating FBC tests with H-Oil conducted at UBC. Filled symbol, velocity = 6.4 m/s; open symbols (exlcuding results for Ca/S = 0), velocity = 8.2-8.8 m/s.

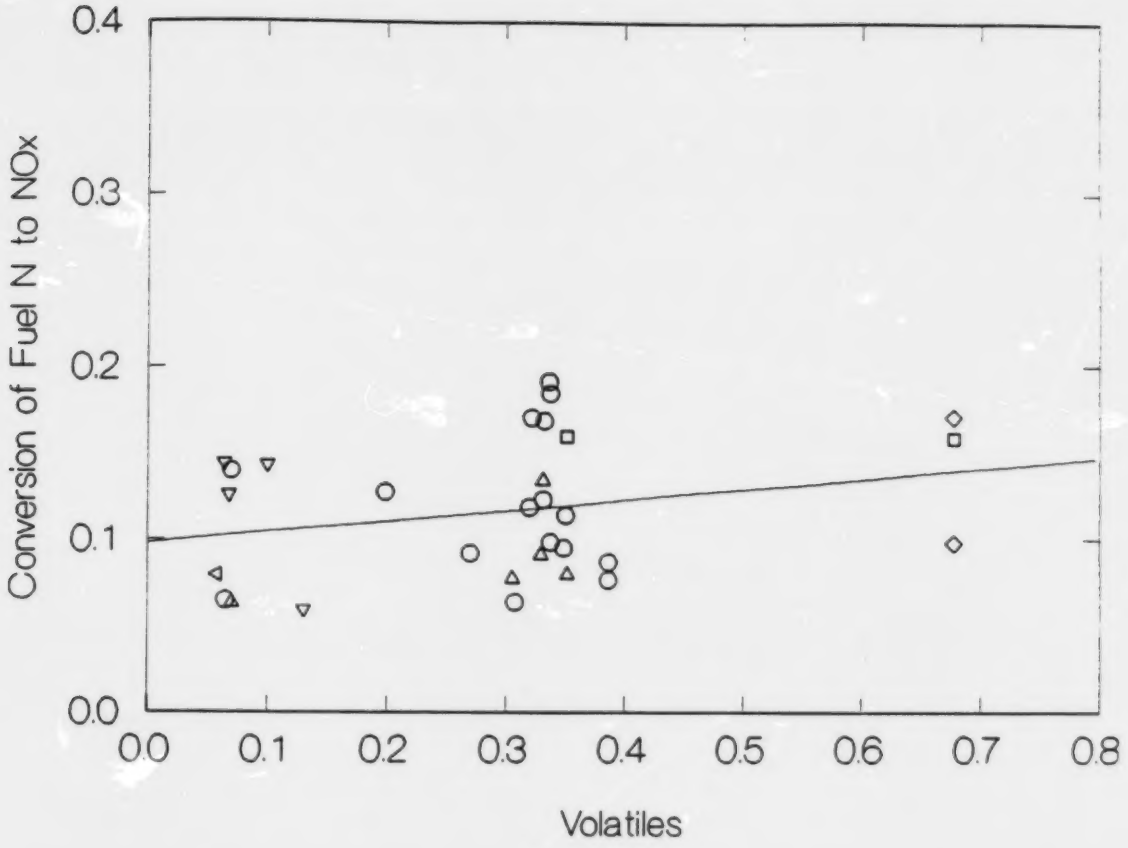

Fig. 12 Effect of fuel volatiles on conversion of fuel N to NO_x.

Legend:
- ○ coal, bubbling FBC
- △ coal, circulating FBC
- ▽ petroleum coke, bubbing FBC
- ◁ petroleum coke, circulating FBC
- □ liquid fuel, bubbling FBC
- ◇ liquid fuel, circulating FBC

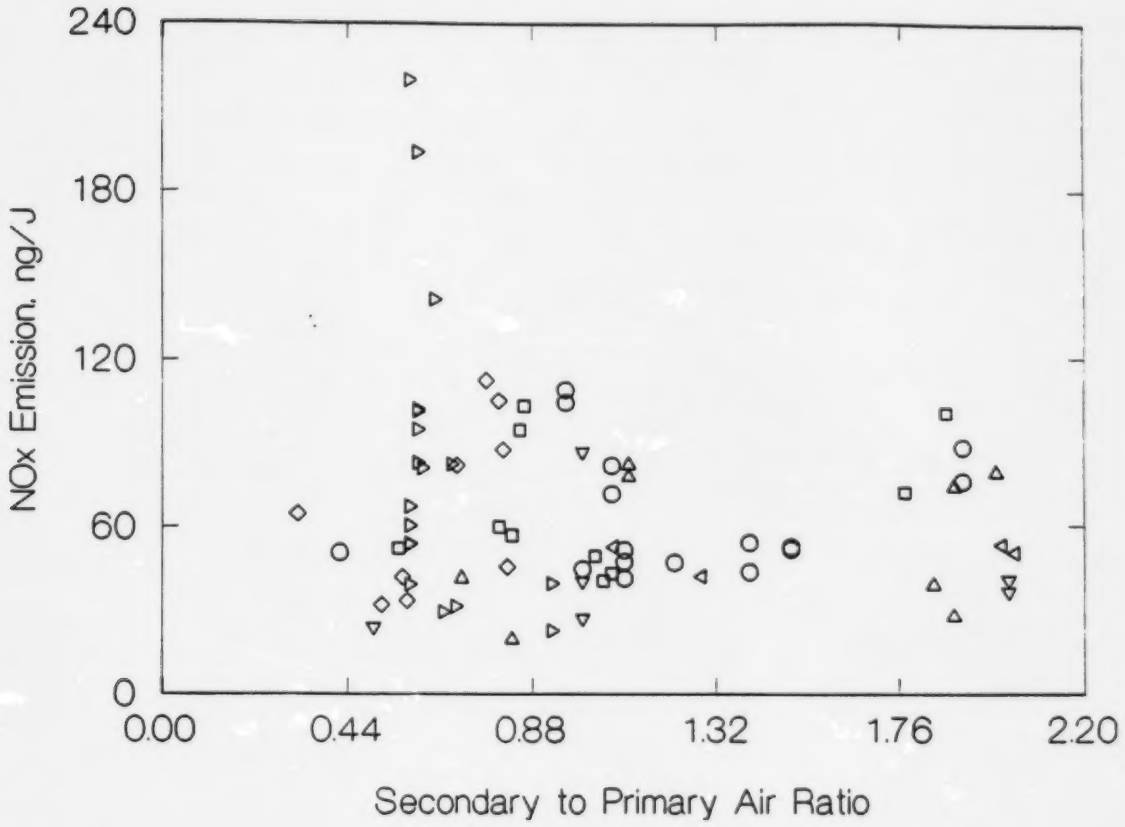

Fig. 13 Effect of secondary air to primary air ratio on NO emission observed in circulating FBC tests.

Legend:

- ○ Minto coal tests at UBC
- △ Highvale coal tests at UBC
- ▽ Mt Klappan coal tests at UBC
- ◁ Poplar River lignite tests at UBC
- ▷ Syncrude coke tests in Finland
- □ CANMET pitch tests at UBC
- ◇ H-oil pitch tests at UBC

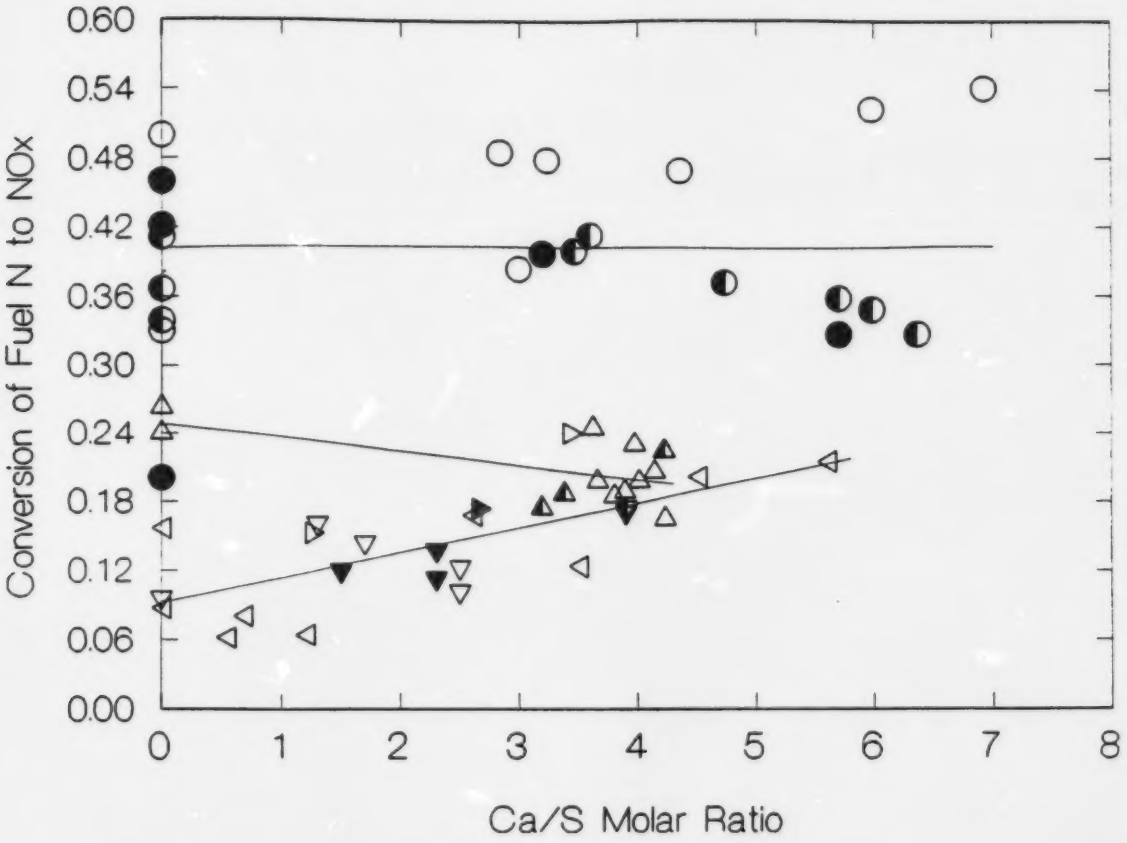

Fig. 14 Effect of Ca/S molar ratio on conversion of fuel N to NO_x of heavy oils.

Legend:
- ○ #6 oil, Mark II BFBC; filled symbols, CO = 1071-3127 ppm; half filled symbols, CO = 502-959 ppm; open symbols, CO = 127-284 ppm
- △ CANMET pitch, Mark II BFBC; filled symbols, CO = 1242-2325 ppm; half filled symbols, CO = 558-857 ppm; open symbols, CO = 273-393 ppm
- ▽ CANMET pitch, UBC CFBC; filled symbols, CO = 700-1000; half filled symbol, CO = 431; open symbols, CO = 120-179 ppm
- ◁ H-oil pitch, UBC CFBC; CO = 124-217 ppm
- ▷ bitumen, Mark II BFBC; filled symbol, CO = 6880 ppm; open symbols, CO = 532-955 ppm